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Journal Item

How to cite:

Shirzadi, A. A.; Koziel, T.; Cios, G. and Bała, P. (2019). Development of Auto Ejection Melt Spinning (AEMS) and its application in fabrication of cobalt-based ribbons. *Journal of Materials Processing Technology* pp. 377–381.

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Version: Version of Record

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1016/j.jmatprotec.2018.09.028>

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Development of Auto Ejection Melt Spinning (AEMS) and its application in fabrication of cobalt-based ribbons



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ARTICLE INFO

Associate editor A. Luo

Keywords:

Melt spinning
Cobalt ribbon
Rapid solidification
Planar flow casting

ABSTRACT

Auto Ejection Melt Spinning (AEMS) is a new variant of melt spinning processes in which spontaneous ejection of the alloy occurs as soon as it is fully melted. Unlike the conventional laboratory melt spinning processes, there is no need for a skilled operator to monitor the melt temperature and/or manually release the ejection gas at the right moment. This new process substantially reduces the uncertainties associated with temperature measurement and human errors. On the request of the authors, the capability of the new process was independently tested and verified by the design engineers of a renowned manufacture of laboratory melt spinners in Germany [Edmund Bühler GmbH]. The application of the new process for fabrication of high melting point cobalt-based ribbons is also described and the key findings are outlined.

1. Introduction

Melt spinning is a method used for rapid solidification of certain alloys mainly to obtain completely non-crystalline ribbons, i.e. amorphous or so-called “metallic glasses”, that cannot be fabricated using conventional continuous casting processes. Depending on the spinning conditions extremely high cooling rates, sufficient to obtain amorphous structures, can be achieved (e.g. tens of thousands of centigrade per second). In this process, first an alloy is melted inside a crucible and then an inert gas is used to flush out the melt through a nozzle, located in the bottom of the crucible, straight onto a rotating copper wheel where it solidifies instantaneously.

Pond and Maddin (1969) used melt spinning as a technique for rapid solidification in their pioneering work. They designed a new apparatus in which a molten alloy was ejected through a sapphire orifice onto the inner surface of a rotating drum. They managed to produce ribbons up to 7 m long and 0.2 mm wide with a thickness of 5–50 microns. Chen and Miller (1970) introduced a new apparatus in which a molten alloy was poured onto a very narrow gap between two counter-rotating rollers. They also studied the effect of the gap size, rotating speed and specimen thermal conductivity on the thickness of ribbons produced. Later Chen and Miller (1976) pointed out that the Pond and Maddin spinner was not suitable for continuous casting as the spun ribbon remains inside the drum. They modified the Pond and Maddin

design by inserting a ring inside the drum in order to guide the ribbon out of the drum continuously. Interestingly 6 decades before Pond and Maddin, Strange and Pim (1908) had designed a melt spinner for production of thin foils of zinc and lead, which is considered to be the origin of conventional copper-wheel melt spinners still in use for rapid quenching. Libermann and Graham (1976) adopted Strange and Pim technique and used Fe₄₀Ni₄₀B₂₀ alloy for production of amorphous ribbons for the first time. In their comprehensive research, they also used Bernoulli equations and other theoretical approaches to demonstrate that the cross-section of spun ribbons is a function of nozzle size, ejection gas pressure, liquid density, wheel diameter and linear speed of the wheel. They also showed that continuous ribbons could be produced if the width to thickness ratio is larger than 5. Fiedler et al. (1984) also used Bernoulli equations and reported that smooth 10 mm wide ribbons could be spun when the nozzle-wheel gap was between 0.1 to 0.15 mm. Swaroopa et al. (2015) studied the effect of ejection pressure and nozzle-wheel gap on the uniformity of spun ribbons using 2D numerical simulation. They concluded that defective ribbons are expected when inadequate ejection pressure results in the formation of so-called “melt puddle pinning to the nozzle slit”. In short, melt spinning is an extremely complex process in which the wheel speed, ejection pressure, nozzle-wheel gap and melt temperature are the most crucial parameters. However, there are other parameters which can affect the shape, uniformity, grain size and surface condition of the final

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<https://doi.org/10.1016/j.jmatprotec.2018.09.028>

Received 20 June 2018; Received in revised form 19 September 2018; Accepted 21 September 2018

Available online 24 September 2018

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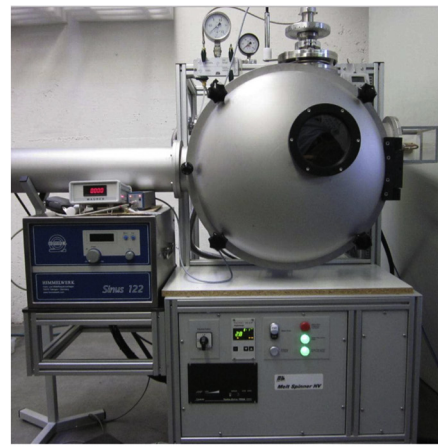
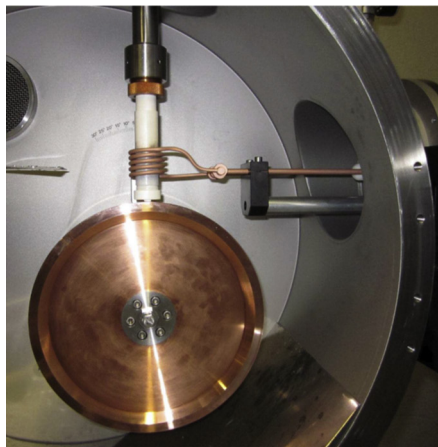


Fig. 1. Melt Spinner used in this work and its peripherals.

product; e.g. nozzle geometry, wheel surface roughness, whether the process is carried out in air or vacuum and even type of the gas used to eject the melt.

In addition to amorphous alloys (e.g. metallic glasses), melt spinning is used for mass production of various ribbons and foils, particularly those which cannot be fabricated using conventional casting and rolling processes. For instance, fabrication of certain brazing foils with non-equilibrium compositions (e.g. containing a high amount of boron) is only possible by melt spinning process. Thin and wide ribbons can be produced by constraining the melt puddle between the nozzle and the surface of rotating copper wheel. In this process, the melt is “drawn out” of the crucible due to the rotation of the wheel if the nozzle is sufficiently close to the wheel surface. The other application of the process is in mass manufacture of thin sheets with extremely small grain sizes. Also, in certain cases where a limited amount of material is needed, melt spinning is a more economical option to conventional rolling due to the much lower capital investment required.

Although melt spinning is widely used for production of certain materials on industrial scales, fabrication of ribbons with high melting points is still a major challenge. Despite a large number of publications on various crystalline alloys, reports on spinning cobalt-based alloys are scant. Saito and Itakura (2013), who studied the magnetic properties of the melt-spun $\text{Co}_{80}\text{Zr}_{20-x}\text{B}_x$ alloys, referred to the difficulties in producing uniform ribbons even on a laboratory scale. Generally, production of uniform and reproducible cobalt-based ribbons by melt spinning proved very difficult if not impossible. The initial aim of this work was to assess the effect of composition and spinning parameters on the uniformity and quality of melt-spun cobalt-based alloys.

2. Problems associated with conventional melt spinning process

Regardless of the type of material used, the temperature of the melt is a critical parameter to obtain sound ribbons. For instance, in order to avoid any superheating, the ejection should start as soon as the material inside the crucible is fully melted. The exceptions are liquid phase-separated alloys. In this family of alloys, overheating above the liquid miscibility gap allows obtaining two-phase amorphous or amorphous + crystalline composites upon cooling.

Four different melt spinners, based in University of Oxford (UK), University of Leoben (Leoben-Austria), Fraunhofer Institute (Dresden-Germany) and AGH University of Science and Technology (Krakow-Poland) were used in connection with this project. The main objective was to achieve high quality cobalt-based ribbons by optimizing the spinning parameters and alloy composition. Regardless of the design and size of the four melt spinners used in this work, all operators had to manually release the ejection gas, based on their experience, in order to fully flush out the molten metal at the right time. A successful process

normally relies on the operator's skill, who visually monitors the temperature and condition of the molten metal inside the crucible. However, most experienced operators would encounter challenges in reading the temperature and deciding on the right moment to release the ejection gas. Besides, visual monitoring of the melt is not possible when using opaque alumina or boron nitride crucibles. Except in industrial melt spinners, in which a large tandish feeds the molten metal into the nozzle, the use of a thermocouple to monitor the temperature during the heating stage can be very erroneous. This is mainly due to the lack of sufficient contact between the thermocouple and solid material inside the crucible, which results in an under-reading of the temperature. This stage is followed by a sudden surge in the temperature reading when the molten metal “engulfs” the thermocouple. Even the melt spinners equipped with advanced pyrometers are susceptible to various errors due to misalignment of the pyrometer and/or gas evolution from the heated material, which can partially “blind” the pyrometer.

In summary, inaccuracy in measuring the temperature and/or human errors can lead to wide variations in the physical and chemical properties of the spun products. This is an accepted fact that the lack of repeatability as well as the dependency on the operator's skill are the main drawbacks associated with melt spinning most materials, particularly the alloys with high melting points and/or wide freezing ranges. In this work, a new method was developed in which the molten metal is ejected out of the crucible without a need for an operator to monitor the temperature and manually release the ejection gas, hence called Auto Ejection Melt Spinning (AEMS). It must be emphasised that AEMS is not a replacement for the automatic valves found in large melt spinners used for mass production. Instead, this new method resolves the uncertainties associated with monitoring the melt temperature in the melt spinners equipped with a gas-ejection system.

3. Experimental procedure

3.1. Conventional melt spinning

Fig. 1 shows the laboratory melt spinner used in this work. The rig operates in a controlled atmosphere and is equipped with an induction heating system. A pressurized gas tank provides the ejection gas needed to flush the molten metal out of the crucible. The wheel speed and the nozzle-wheel gap are fully adjustable.

The main steps when using laboratory melt spinners, similar to the one shown in Fig. 1, are as follows:

- 1 About 10–30 g of the alloy is placed in the boron nitride (BN) crucible with a slit-shape nozzle in the bottom.
- 2 The crucible is mounted inside the induction heating coil and

aligned relative to the copper wheel. The gap between the nozzle and copper wheel (normally around 0.2–0.6 mm) is a crucial parameter; therefore, it must be carefully adjusted using a feeler gauge.

- 3 A pyrometer is placed above the rig and aligned to measure the temperature of the material inside the crucible (in some spinners a thermocouple is inserted inside the crucible).
- 4 The chamber is evacuated down to 10^{-4} to 10^{-5} mbar and the spinning speed of the copper wheel is set depending on the composition, thickness and properties of the ribbon to be spun.
- 5 Once the material is fully melted, judged visually or by monitoring the temperature, the operator opens a valve to release the ejection gas into the crucible and discharge the molten metal straight onto the spinning copper wheel. The entire ejection stage lasts two to three seconds when spinning 20–30 g of alloy.

As mentioned above, most operators rely on visual observation to determine whether the material inside the crucible is fully melted before opening the ejection valve. This practice is even more difficult, and sometime impossible, when the crucible is made of an opaque material such as alumina or boron nitride. The poor repeatability of such tests proved to be due to the uncertainty in measuring the melt temperature and also inconsistency in determining the optimum ejection time. In some cases, the melt was overheated and in other cases it was partially melted. For instance, in this work, overheating resulted in the cobalt ribbons with undesirable properties and also damaged the boron nitride crucible. On the other hand, when the ejection valve was opened too early, most of the partially melted alloy remained in the crucible.

3.2. Auto Ejection Melt Spinning (AEMS)

A new method was developed in this work to avoid the overheating or underheating issues. The main objective was to improve the thickness and uniformity of the spun ribbons by ejecting the alloy as soon as it is fully melted and without operator's intervention. In this new method, the pre-ejection steps are identical to those used the conventional method as listed above. However, in order ensure the feed alloy is uniformly melted, it is essential to avoid large temperature gradients inside the crucible by using low heating rates. Once the temperature of the material reached about 200 °C below its melting point, a gentle stream of nitrogen or argon is directed into the crucible. The flow rate of the gas needs to be controlled using an in-line flow meter. The optimum flow rate depends on the size of crucible and is expected to be between 200–800 cubic centimeters per minute. Once the flow rate is adjusted, the rest of the process would not require any intervention by the operator. Initially, the gas gently bypasses the solid material inside the crucible and exits through the nozzle, expanding gradually into the vacuum chamber. However, this is a transient stage and as soon as the alloy is melted, the nozzle is blocked and consequently the pressure inside the crucible increases rapidly. Within a few seconds the pressure inside the crucible reaches a critical level, which is sufficient to flush out the melt through the nozzle. The key stages of Auto Ejection Melt Spinning (AEMS) process are shown in Fig. 2 and outlined below.

Stage 1: An inert gas with a very low flow-rate bypasses the solid alloy inside the crucible.

Stage 2: The alloy is melted; the nozzle is blocked and the pressure inside the crucible increases rapidly.

Stage 3: Pressure above the melt reaches a critical level and the molten metal is ejected through the nozzle onto the rotating copper wheel.

Fig. 3 shows a picture, taken by a high-speed camera, of the auto ejection moment of the cobalt-based alloy used in this work. The capability of the new process was independently tested and verified by a renowned manufacture of laboratory melt spinners in Germany [Edmund Bühler GmbH].

4. Case study: melt spinning of cobalt-based alloys

The authors were involved in a comprehensive R&D project on the melt spinning of cobalt ribbons containing up to 7 wt.% Fe, 1.5 wt.% Mn and 0.7 wt.% Si. About 150 tests were carried out to assess the effect of process parameters on various properties of the spun ribbons. The main process parameters were melt temperature, ejection pressure, chamber atmosphere (various gases and vacuum), linear speed of the copper wheel, gap between the nozzle and the wheel and nozzle size. The effects of adding small amounts of nickel and a rare earth element (cerium) on the microstructure of the ribbons were also researched. The detailed outcome of the project is not within the scope of this paper, nevertheless, the main challenges and findings of the work are outlined below.

4.1. Selection of a suitable crucible

Differential scanning calorimetry (DSC) showed that the Co-Fe-Mn-Si alloy had a melting point around 1500 °C. The use of conventional quartz crucibles proved unsuccessful due to their softening and excessive elongation despite short holding times at high temperatures. Excessive elongation of the quartz crucibles made it impossible to maintain a constant gap between the nozzle and the copper wheel.

Hence, most of the tests were carried out using a modular crucible made of boron nitride as shown in Fig. 4. Each crucible consisted of a tube, a 2-piece slit nozzle and a screw ring, which holds the nozzle beneath the tube - see the setup in Fig. 1. Despite expected endurance of boron nitride (BN) at temperatures up to 1800 °C in vacuum, substantial reaction between the molten cobalt alloy and boron nitride resulted in fast erosion and deterioration of the nozzle. According to the experts in handling this family of molten alloys, alumina would be the most suitable crucible material when melt spinning cobalt alloys, despite its lower impact resistance compared to boron nitride. Therefore, use of boron nitride crucibles for mass melt spinning of cobalt alloys with such a high melting point is not recommended.

4.2. Summary of key findings

- I Development of dendritic structure in cobalt ribbons is undesirable because it leads to the formation of discontinuities such as hot cracks.
- II Increasing the cooling rate and /or reducing ejection temperature and/or keeping the ribbon in contact with the wheel for a longer time can reduce hot cracking.
- III Selection of the ambient atmosphere is utmost important. Conventional spinning in vacuum resulted in low quality ribbons. In contrast, the best ribbons were produced using the auto-ejection process and CO₂. It must be emphasised that the quality and uniformity of melt-spun ribbons depend on many parameters. The key advantage of the auto-ejection process is in resolving the uncertainties associated with temperature measurement and human errors.
- IV The effect of addition of various elements on the solidus and liquidus temperatures of the base Co-Fe-Mn-Si alloy was simulated using MTDATA Software and the results are shown in Fig. 5. Based on phase diagram modelling and a number of experimental trials, it was shown that addition of 2–3% nickel reduces the grains size. Fig. 6 shows the cobalt ribbons containing about 3% nickel had fine equiaxed grains with no or limited amounts of dendrites or cracks. This is probably due to the change in the solidification range of the alloys by addition of nickel.
- V The addition of 0.12–0.45 atomic percent of cerium had no effect on the microstructure or quality of the ribbons.
- VI Optimum spinning speed and nozzle-wheel gap were about 5 m/s and 0.3–0.4 mm, respectively. However, these values may vary depending on the crucible size, spinning temperature and ejection

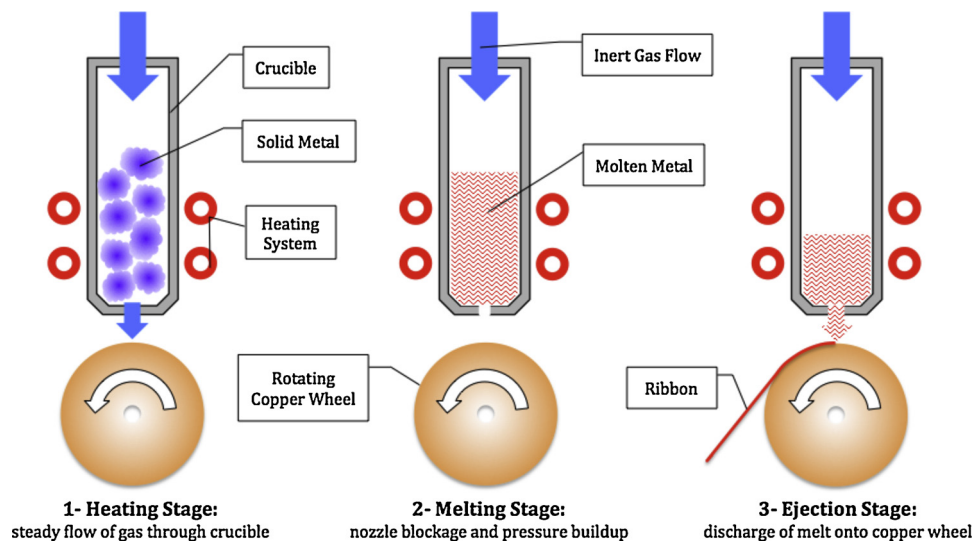


Fig. 2. Graphical demonstration of Auto Ejection Melt Spinning (AEMS) stages.

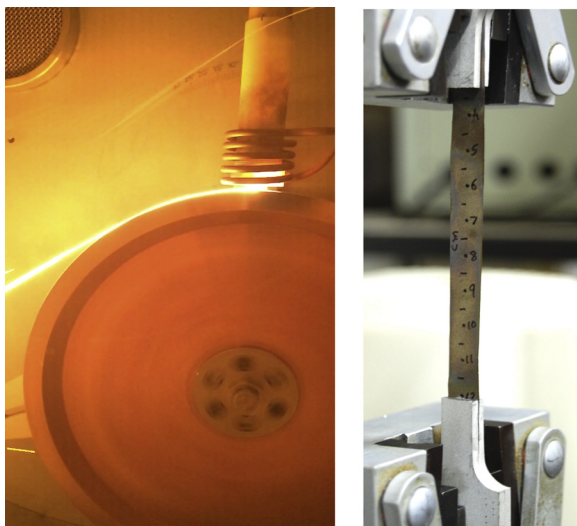


Fig. 3. Auto Ejection Melt Spinning (AEMS) of a cobalt alloy at about 1500 °C was captured using a high-speed video camera. A special fixture was made and used for tensile testing of the melt spun ribbons.



Fig. 4. Modular boron nitride crucible used in this work (courtesy Edmund Bühler, Germany).

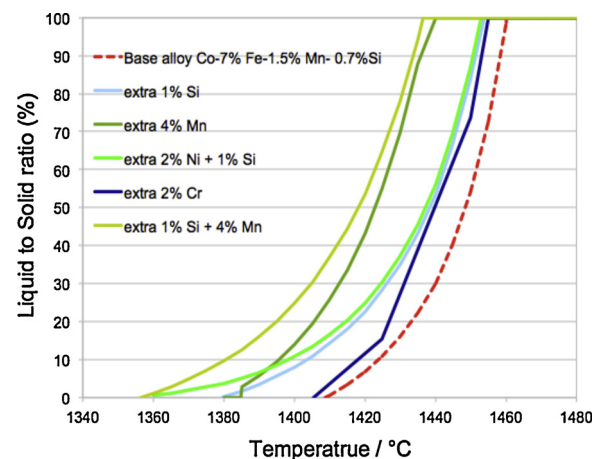


Fig. 5. Effect of addition of Si, Mn, Ni and Cr on solidification range of base Co alloy calculated using MTDATA phase diagram Software developed by the UK National Physical Laboratory.

pressure.

VII Maximum tensile strength and ductility of the base cobalt alloy, when spun in CO₂, were 138 MPa and 12.5%, respectively. The setup used for tensile testing of the ribbons is shown in Fig. 3.

VIII Ductility of the nickel-containing ribbons, spun in the same condition, was about 11% lower than that of the base alloy ribbons. This is an unexpected outcome since a ribbon with finer grains should have higher ductility. However, SEM microscopy at higher magnifications revealed the presence of very small defects within the fine grains. Fig. 7 shows the nickel-containing ribbon has 3–5 micron-size voids, which could not be seen in the optical micrographs shown in Fig. 6.

IX It must be noted that 20–30 g of samples were spun in each run, hence only short ribbons up to 2 m long and 10 mm wide could be produced. Mechanical properties of the test samples taken from the center part of longer ribbons are expected to be better. This is because of much higher density of defects normally found in the head and tail sections of ribbons regardless of the spinning parameters.

5. Conclusions

Auto Ejection Melt Spinning (AEMS) is a new process which was

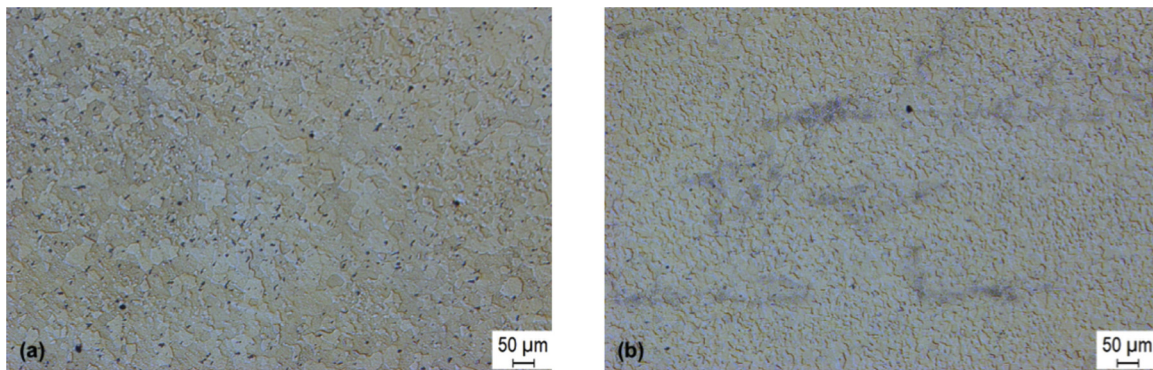


Fig. 6. Optical micrographs show addition of nickel resulted in grain refinement of melt spun ribbon; (a) base alloy and (b) base alloy plus ~ 3 wt.% Ni.

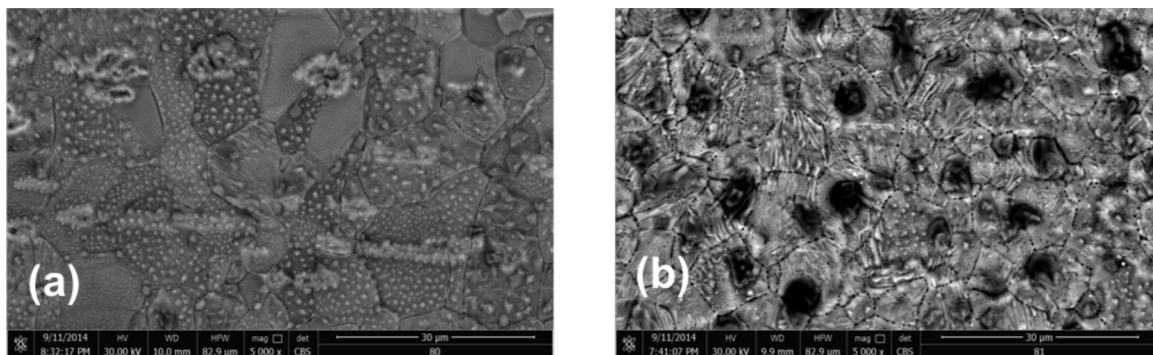


Fig. 7. SEM micrographs show the grains in a melt-spun base alloy (a) are larger than in the nickel-containing alloy (b). However, the nickel-containing ribbon has much more micron-size voids and defects.

developed in this work in order to improve the performance and repeatability of the melt spinners equipped with gas ejection systems. This new process eliminates the errors associated with measuring the melt temperature, since the ejection occurs spontaneously and as soon as the alloy inside the crucible is fully melted.

A major manufacture of laboratory melt spinners in Germany [Edmund Bühler GmbH] independently tried and verified the capability of the new process by using their own melt spinner.

The exemplary properties of a melt-spun cobalt alloy were used to verify the effectiveness of this new process in fabrication of high strength ribbons without intervention by the operator.

Acknowledgements

The project was financially supported by Welding Alloys France SAS. The first author is grateful for the support received from Guangdong Innovative and Entrepreneurial Research Team Program (Project No. 2016ZT06G025).

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